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(64) Combination process for making improved lubricating oils from marginal crudes.

(57) Light and air stable lubricating oils with a viscosity index in the order of 100 are produced from marginal crude feedstocks in a combination process consisting of 1) solvent, e.g., furfural, extraction, 2) catalytic dewaxing and 3) catalytic hydrotreating. Catalytic hydrotreating the dewaxed lube at pressures of 6996-20786 kPa (1000-3000 psig) to a viscosity index of 100 coincides with essentially complete desulfurization.

COMBINATION PROCESS FOR MAKING IMPROVED  
LUBRICATING OILS FROM MARGINAL CRUDES

This invention is concerned with manufacture of high grade viscous oil products from crude petroleum fractions. It is particularly directed to the manufacture of high quality lube basestock oils from crude stocks of high wax content, commonly classified as "wax base" as compared with the "naphthenic base" crudes. The latter crudes are relatively lean and straight chain paraffins and yield viscous fractions which inherently possess low pour points. More specifically, the invention is concerned with improving the viscosity index of lube basestock oils obtained from marginal lube crudes.

High quality lube basestock oils are conventionally prepared by refining distillate fractions or the residuum prepared by vacuum distilling a suitable crude oil from which the lighter portion has been removed by distillation in an atmospheric tower. Thus, the charge to the vacuum tower is commonly referred to as a "long residuum" and residuum from the vacuum tower is distinguished from the starting material by referring to it as the "short residuum".

The vacuum distillate fractions are upgraded by a sequence of unit operations, the first of which is solvent extraction with a solvent selective for aromatic hydrocarbons. This step serves to remove aromatic hydrocarbons of low viscosity index and provides a raffinate of improved viscosity index and quality. Various processes have been used in this extraction stage, and these employ solvents such as furfural, phenol, sulfur dioxide, and others. The short residuum, because it contains most of the asphaltenes of the crude oil, is conventionally treated to remove these asphalt-like constituents prior to solvent extraction to increase the viscosity index.

The raffinate from the solvent extraction step contains paraffins which adversely affect the pour point. Thus, the waxy raffinate, regardless of whether prepared from a distillate fraction or from the short residuum, must be dewaxed. Various dewaxing procedures

have been used, and the art has gone in the direction of treatment with a solvent such as methyl ethyl ketone/toluene mixtures to remove the wax and prepare a dewaxed raffinate. The dewaxed raffinate may then be finished by any number of sorption or catalytic processes to improve color and oxidation stability.

The quality of the lube basestock oil prepared by the sequence of operations outlined above depends on the particular crude chosen as well as the severity of treatment for each of the treatment steps. For example, crudes such as Arab Heavy have been found previously to be unsatisfactory crudes for making lubes having a viscosity index (V.I.) of 100 using conventional furfural extraction and solvent dewaxing processing steps and are thus characterized as giving marginal quality lubricating oils. Additionally, the yield of high quality lube basestock oil also depends on these factors, and as a rule, the higher quality sought, the less the yield. In general, naphthenic crudes are favored because less loss is encountered, particularly in the dewaxing step. In many cases, however, waxy crudes are more readily available, and it would be desirable to provide a process for preparing high quality lube basestock oils in good yields from such waxy crude oils to broaden the crude sources for making lubes.

In recent years techniques have become available for catalytic dewaxing the petroleum stocks. A process of that nature developed by British Petroleum is described in the Oil and Gas Journal dated January 6, 1975, at pages 69-73. See also U. S. Patent No. 3,668,113.

In U. S. Patent No. Reissue 28,398 is described a process for catalytic dewaxing with a catalyst comprising zeolite ZSM-5. Such process combined with catalytic hydrofinishing is described in U. S. Patent No. 3,894,938 for reducing the pour point of a sulfur and nitrogen-containing gas oil boiling within the range of 400-900°F (204-482°C).

In U. S. Patent No. 3,979,279, a stabilized lubricating oil stock resistant to oxidation and sludge formation upon exposure to a highly oxidative environment is formed by contacting a high viscosity lubricating oil stock with hydrogen in the presence of a catalyst of low acidity comprised of a platinum- group metal on a solid refractory inorganic oxide support.

In U. S. Patent No. 3,530,061, a stabilized lube oil product obtained by hydrocracking is produced by contacting a lube oil product before or after dewaxing with a catalyst having hydrogenation-dehydrogenation activity and hydrogen at a pressure in the range from atmospheric up to about 100 psig (791 kPa) under conditions of temperature in the range of 400°F (204°C) to about 800°F (427°C).

A two-stage process for preparing a high quality lube basestock oil is disclosed in U. S. Patent No. 4,181,598 in which a raffinate is mixed with hydrogen and the mixture contacted with a dewaxing catalyst comprising a ZSM-5 type catalyst to convert the wax contained in the raffinate to low boiling hydrocarbons and subsequently, contacting the dewaxed raffinate in the presence of hydrogen at a temperature of 425-600°F (218-316°C) with a hydrotreating catalyst comprising a hydrogenation component on a non-acid support such as cobalt-molybdate or nickel-molybdate on alumina. Hydrotreating the dewaxed raffinate is limited to saturate olefins and reduce product color without causing appreciable desulfurization.

It has been found in a hydrofinishing optimization study that at higher temperatures above 500°F (260°C) oxidation stability declined but that the viscosity index could be increased several numbers.

It is an object of this invention to provide a process for increasing the viscosity index of a dewaxed lube basestock oil obtained from marginal crudes in order to broaden the crude sources for making lubes.

Another object of the invention is to produce light and air stable lubricating oils with V.I. in the order of 100 from marginal crude feedstocks. Other objects will be evident to those skilled in the art upon reading the entire contents of this specification, including the claims thereof.

The present invention provides a process for preparing a high quality lube basestock oil from waxy crude oil. Such a process comprises (A) extracting a waxy crude oil distillate fraction that boils within the range of from 316°C to 593°C (600°F to 1100°F), or a deasphalted short residuum fraction of such a waxy crude oil, with an aromatic hydrocarbon solvent in order to yield a wax-containing raffinate from which

undesirable compounds have been removed; (B) mixing the wax-containing raffinate with hydrogen and contacting this mixture under particular temperature conditions with a particular type of dewaxing catalyst to thereby convert wax contained in the raffinate to lower boiling hydrocarbons; and (C) cascading this dewaxed raffinate to a hydrotreating zone wherein the dewaxed raffinate is contacted in the presence of hydrogen with a particular type of hydrotreating catalyst under particular reaction conditions to hydrotreat the dewaxed raffinate to substantially complete desulfurization but to avoid substantial hydrogenation of aromatic compounds in the raffinate. Such a procedure yields a lube basestock oil having a viscosity index of approximately 100.

The dewaxing catalyst employed in the dewaxing step is a catalyst comprising an aluminosilicate zeolite having a silica/alumina ratio of at least 12 and a constraint index of from 1 to 12. Temperature in the dewaxing step ranges from 260°C to 357°C (500°F to 675°F).

The hydrotreating catalyst employed in the hydrotreating zone comprises a strong hydrogenation component on a non-acidic support. Conditions in the hydrotreating zone include a hydrogen partial pressure of from about 6996 kPa to 20786 kPa (1000 psig to 3000 psig), a temperature of from about 260°C to 357°C (500°F to 675°F) and a liquid hourly space velocity of from about 0.1 to 2.0.

The present invention is thus based on the discovery that the obtainable light and air stability and high viscosity index of the resulting product coincides with essentially complete desulfurization of this dewaxed lube product. Light and air stable lubricating oils with a viscosity index in the order of 100 can thus be produced from marginal crude feedstocks.

The features of the present invention can be illustrated by Figures 1-5 of the drawings discussed more fully hereinafter.

Figure 1 is a graph of experimental data illustrating lube yield after hydrotreating versus viscosity index of the lube product.

Figure 2 is a graph of experimental data illustrating sulfur content versus viscosity index of the hydrotreated lube product.

Figure 3 is a graph of experimental data illustrating hydrogen consumption versus viscosity index of the hydrotreated lube.

Figure 4 is a graph of experimental data illustrating pour point versus viscosity index of the hydrotreated lube.

Figure 5 is a graph of experimental data illustrating viscosity versus viscosity index.

The wax base crudes (sometimes called "paraffin base") from which the chargestock is derived by distillation constitute a well-recognized class of crude petroleum. Many scales have been devised for classification of crude, some of which are described in chapter VII, Evaluation of Oil Stocks of "Petroleum Refinery Engineering," W. L. Nelson, McGraw Hill, 1941. A convenient scale identified by Nelson at page 69 involves determination of the cloud point of the U.S. Bureau of Mines (key fraction #2) which boils between 527°F (275°C) and 572°F (300°C) at 40 mm (5333 Pa) pressure. If the cloud point of this fraction is above 5°F (-15°C), the crude is considered to be wax base.

In practice of the present invention, a suitable chargestock such as a propane deasphalted short residuum fraction or a fraction having an initial boiling point of at least about 450°F (232°C), and preferably at least about 600°F (316°C), and a final boiling point less than about 1100°F (593°C) is prepared by distillation of such wax base crude. Such fraction can then be solvent refined by counter current extraction with at least an equal volume (100 volume percent) of a selective solvent such as furfural. It is preferred to use about 1.5-3.0 volumes of solvent per volume of oil. The solvent, e.g., furfural, raffinate can be subjected to catalytic dewaxing by mixing with hydrogen and contacting at 500-675°F (260-357°C) with a catalyst containing a hydrogenation metal and zeolite ZSM-5 or other related silicate zeolites having a silica/alumina ratio of at least 12 and a Constraint Index of 1-12 using a liquid hourly space velocity (LHSV) of 0.1-2.0 volumes of charge oil per volume of catalyst per hour. The preferred space velocity is 0.5-1.0 LHSV.

The effluent of catalytic dewaxing can then be cascaded into a hydrotreater containing, as catalyst, a strong hydrogenation component on a non-acid support, such as supported nickel-tungsten or platinum on alumina. Typically, the hydrotreater operates at temperatures of

500-675°F (260-357°C) and at elevated pressures within the range of 1000-3000 psig (6996-20786 kPa), preferably 1200-2500 psig (8375-17338 kPa) and a space velocity like that of the catalytic dewaxing reactor.

The catalytic dewaxing reaction can be carried out at hydrogen partial pressures of 150-3000 psia (1034-20684 kPa), at the reactor inlet, and preferably at 250-1500 psia (1724-10342 kPa). Dewaxing and hydrotreating operate at 500 to 5000 standard cubic feet of hydrogen per barrel of feed (SCF/bbl) (89 to 890 nl of  $H_2$ /l of feed), preferably 1500-2500 SCF/bbl (267-445 nl/l). It is preferred to dewax at the same pressure as the hydrotreat stage.

At the conditions utilized in the hydrotreater, the dewaxed effluent is converted over the strong hydrogenating catalyst to a material having a viscosity index (V.I.) of approximately 100, e.g., from 95 to 105. The viscosity index is an empirical number indicating the effect of change of temperature on the viscosity of an oil. A low viscosity index signifies a relatively large change of viscosity with temperature, and vice versa. By means of the viscosity index function, the steepness of the viscosity-temperature curve of the sample is interpolated between that of a Pennsylvania Oil (denoted as 100 VI) and that of a Texas Coastal Oil (denoted 0 VI), both of which reference oils have the same viscosity as the sample at 210°F (99°C).

The high viscosity index of the lube obtained coincides with substantially complete desulfurization. While further cracking increases V.I., loss of yield increases and both light and air stability suffer.

In some instances, it may be desirable to partially dewax the chargestock, i.e., solvent-extracted raffinate, by conventional solvent dewaxing techniques, say to a pour point from 10°F (-12°C) to about 50°F (10°C). The higher melting point waxes so removed are those of higher market value than the waxes removed in conventionally taking the product to a still lower pour point below 10°F (-12°C).

The cracked (and hydrogenated) fragments from cracking wax molecules in the catalytic dewaxer will have adverse effects on flash and fire points of the dewaxed raffinate product and are therefore removed by distillation of the product to flash and fire point specifications.

The catalyst employed in the catalytic dewaxing reaction zone and the temperature in that reaction zone are important to success in obtaining good yields and very low pour point product. The strong hydrotreater catalyst may be any of the catalysts commercially available for that purpose but the temperature should be held within narrow limits for the desired cracking (desulfurization).

The solvent extraction technique is well understood in the art and needs no detailed review here. The severity of extraction is adjusted to composition of the chargestock to meet specifications for the particular lube basestock and the contemplated end-use; this severity will be determined in practice of this invention in accordance with well established practices.

The catalytic dewaxing step can be conducted at temperatures of 500-675°F (260-357°C). At temperatures above about 675°F (357°C), bromine number of the product generally increases significantly and the oxidation stability decreases.

The dewaxing catalyst is preferably a composite of hydrogenation metal, preferably a metal of Group VIII of the Periodic Table, associated with the acid form of an aluminosilicate zeolite having a silica/alumina ratio of at least about 12, and a constrained access to the intracrystalline free space as measured by having a Constraint Index of from about 1 to 12.

Zeolite materials of silica/alumina molar ratio greater than 12 and Constraint Index of 1 to 12 are used in the dewaxing catalyst employed in the present invention. Such zeolites, also known as ZSM-5 type zeolites, are well known. This use as dewaxing catalysts has, for example been described in U.S. Patent 4,358,363.

Crystalline zeolites of the type useful in the dewaxing catalysts of the present invention include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 and zeolite beta, with ZSM-5 being particularly preferred.

ZSM-5 is described in greater detail in U.S. Patent Nos. 3,702,886 and RE 29,948, which patents provide the X-ray diffraction pattern of the therein disclosed ZSM-5.



ZSM-11 is described in U.S. Patent No. 3,709,979, which discloses in particular the X-ray diffraction pattern of ZSM-11.

ZSM-12 is described in U.S. Patent No. 3,832,449, which discloses in particular the X-ray diffraction pattern of ZSM-12.

ZSM-23 is described in U.S. Patent No. 4,076,842, which discloses in particular the X-ray diffraction pattern of ZSM-23.

ZSM-35 is described in U.S. Patent No. 4,016,245, which discloses in particular the X-ray diffraction pattern of ZSM-35.

ZSM-38 is described in U.S. Patent No. 4,046,859, which discloses in particular the X-ray diffraction pattern of ZSM-38.

ZSM-48 is described in U.S. Patent No. 4,375,573 and European Patent Publication EP-A-0015132, which discloses in particular the X-ray diffraction pattern of ZSM-48.

Zeolite beta is described in greater detail in U.S. Patent Nos. 3,308,069 and RE 28,341, which patents disclose in particular the X-ray diffraction pattern of zeolite beta.

A ZSM-5 type zeolite also useful herein includes the highly siliceous ZSM-5 described in U.S. Patent 4,067,724 and referred to in that patent as "silicalite."

The specific zeolites described, when prepared in the presence of organic cations, are catalytically inactive, possibly because the intracrystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert atmosphere at 1000°F (538°C) for 1 hour, for example, followed by base exchange with ammonium salts followed by calcination at 1000°F (538°C) in air. The presence of organic cations in the forming solution may not be absolutely essential to the formation of this type zeolite; however, the presence of these cations does appear to favor the formation of this special type of zeolite. More generally, it is desirable to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about 1000°F (538°C) for from about 15 minutes to about 24 hours.

Thus when synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, generally by intermediate formation of the ammonium form as a result of ammonium form to yield the

hydrogen form. In addition to the hydrogen form, other forms of the zeolite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used. In this manner, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable ions of Groups IB to VIII of the Periodic Table, including, by way of example, nickel, copper, zinc, palladium, calcium or rare earth metals.

In practicing the catalytic dewaxing step of the present invention, it may be desirable to incorporate the above-described crystalline aluminosilicate zeolite in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic or naturally occurring substances as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which can be composited with the zeolite include those of the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the zeolites employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions, such as silica-alumina-thoria, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and matrix may vary widely with the zeolite content ranging from between about 1 to about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the composite.

In the process of this invention, the total effluent of the catalytic dewaxing step, including the hydrogen, is cascaded into a hydrotreating reactor of the type now generally employed for finishing of

lubricating oil stocks. In this "cascade" mode of operation, the hydrotreater is sized to handle the total dewaxer effluent. Although some modification of the cascade operation is contemplated, such as interstage recovery of gasoline boiling range by-product, it is to be understood that such modification contemplates no substantial interruption or substantial delay in passing the dewaxed raffinate to the hydrotreater. Thus, "cascading", as used herein, means passing the dewaxed raffinate plus hydrogen to hydrotreating without storage of the dewaxer effluent.

Any of the known hydrotreating catalysts consisting of a strong hydrogenation component on a non-acidic support may be employed in the hydrotreating step. Such catalysts include, for example, nickel-tungsten on silica-alumina or platinum on alumina. Here again, temperature control is required for production of high quality products having the desired desulfurization and thus high V.I as well as light and air stability.

The effluent of the hydrotreater is topped by distillation, i.e., the most volatile components are removed, to meet flash and fire point specifications.

The following Examples are given as illustrative of this invention and are not to be construed as limiting thereon except as defined by the claims. In the Examples, all parts are given by weight unless specified otherwise.

#### Example 1

The crude source of this Example is Arab Heavy. Distillation of the crude yielded 9.1% volume vacuum distillate, above a 27.3% volume vacuum resid. The vacuum distillate had the properties as set forth in Table 1.

TABLE 1Properties of Distillate

Gravity, °API	18.4
Specific	0.944
Distillation	
IBP*	615°F (324°C)
5%	797°F (425°C)
10	843°F (451°C)
30	875°F (468°C)
50	895°F (479°C)
70	918°F (492°C)
90	960°F (516°C)
95	983°F (528°C)
Composition	
Paraffins	16% by weight
Naphthenes	23% by weight
Aromatics	61% by weight

\*Initial Boiling Point

The vacuum distillate was furfural extracted at 195°F using a solvent/oil ration of 200. The yield of raffinate was 53.3 wt.% and had the following properties:

Gravity, °API	27.4
Specific	0.8905
KV* at 100°C, centistokes	9.58
Refractive Index at 70°C	1.4704

\*Kinematic Viscosity

The raffinate obtained above was processed under dewaxing conditions to a pour point of +25°F (-4°C) using a dual catalyst bed of Ni/ZSM-5 followed by Co/Mo/Al. The dewaxing conditions are as follows:

Pressure, psig	400 (2859 kPa)
LHSV	1.0 hr <sup>-1</sup>
H <sub>2</sub> Circ., SCF/bbl	2500 (445 nl/l)
Temp., °F	500-675 (288-357°C) (Ni/ZSM-5)
	515 (268°C) (Co/Mo/Al)

Yield of the dewaxed oil was 84.7 wt.%. The properties of the product are set forth in Table 2.

TABLE 2

Properties of Dewaxed Lube

Gravity, °API	26.0
Specific	0.8984
Pour Point, °F	+25 (-4°C)
KV* at 40°C, cs	116.1
100°C, cs	11.47
SUS** at 100°F, Sec.	611
210°F, Sec.	65.7
Viscosity Index	82.5
Sulfur, wt.%	1.19
Wt.% S Compounds	17***
Boiling Range, °F	
1%	617 (325°C)
5	749 (398°C)
10	790 (421°C)
30	849 (454°C)
50	884 (473°C)
70	916 (491°C)
90	961 (516°C)
95	984 (529°C)

\*Kinematic Viscosity

\*\*Saybolt Universal Seconds

\*\*\*Assuming one S atom/molecule

The viscosity index of the oil is too low to be of commercial value as is that obtained by conventional solvent dewaxing of the raffinate (about 90). In addition, the viscosity of the catalytically dewaxed oil is undesirably high.

Example 2

The catalytically dewaxed oil of Example 1 having the properties set forth in Table 2 was hydrotreated over a commercial catalyst Ni/W/Ti/SiAl (ICR-106™ from Chevron). The catalyst samples contained 19.7 wt.% W, 6.5 wt.% Ni, 4.5 wt.% Ti, 0.04 wt.% CoO, 0.03 wt.% MoO<sub>3</sub>, and the remainder is silica- alumina. The catalyst was sulfided before use. Conditions of the hydrotreating were as follows:

Pressure, psig	1500 (10443 kPa)
LHSV, hr <sup>-1</sup>	0.5
H <sub>2</sub> Circ., SCF/bbl	5000 (890 nl/l)
Temp., °F	525-650 (274-343°C)

Hydrogen circulation, pressure and LHSV were kept constant while the temperature was varied. Detailed run data using ICR-106™ is set forth in Table 3.

TABLE 3  
Run Data, TOR-106™

Run No. Time On Stream, days Temperature, °F, Average Maximum	Charge							
	Catalyst Conditions		Arab Heavy Refillinate, NI/M/TI/StAl 1500 psia, 0.5 LHSV, 5000 SCF H <sub>2</sub> /bbl					
	C	H	A	R	G	E		
	-1	-2	-3	-4	-5	-6	-7	-8
	0.9	1.8	2.7	3.6(1)	4.5	5.5	6.4(1)	7.3
	600	551	550	525	576	599	652	651
	603	553	553	527	579	601	654	654
Run Time, hrs	20.5	22.5	22.5	22.5	22.5	22.5	2	23
Liquid Product Gravity, °API	52.3	33.7	30.1	28.1	28.6	29.6	33.7	40.6
Material Balance, wt %	94.0	101.8	100.3	100.1	100.4	100.7	99.5	95.2
Yields, wt % (NLB)								
Cl+C <sub>2</sub>	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
C <sub>3</sub>	1.4	0.1	0.1	<0.1	<0.1	<0.1	0.1	0.4
C <sub>4</sub>	7.2	0.9	0.1	<0.1	0.1	<0.1	0.3	1.2
C <sub>5</sub>	0.7	0.1	0.1	<0.1	0.1	<0.1	0.1	0.9
C <sub>6</sub> -650°F	5.8	18.6	7.3	1.8	2.5	2.4	15.7	41.3
650°F+ Lube	86.2	78.9	91.7	97.8	96.7	96.7	83.1	56.2
H <sub>2</sub>	1.3	1.2	0.9	0.5	1.0	1.1	1.2	1.3
Total	102.0	100.4	100.1	100.1	100.2	100.2	100.5	101.3
Hydrogen Cons., SCF/bbl	1175	200	50	60	120	105	275	740
650°F+ Lube Properties								
Gravity, °API	26.0	30.1	28.3	27.1	28.3	27.4	30.9	34.5
Specific	0.8984	0.8756	0.8655	0.8722	0.8855	0.8905	0.8713	0.8524
Pour Point, °F	+25	+25	+20	+20	+25	+25	+30	+20
KV @ 40°C, cs	116.1	64.30	86.44	103.60	93.67	89.42	63.33	36.13
KV @ 100°C, cs	11.47	9.82	9.82	10.82	10.26	10.00	8.33	6.03
KV @ 100°F, cs (Calc.)	131.8	71.82	97.34	117.2	105.7	100.8	70.70	39.79
KV @ 210°F, cs (Calc.)	11.81	8.61	10.10	11.13	10.55	10.28	8.55	6.17
SUS @ 100°F	611	333	451	543	490	467	328	185.8
SUS @ 210°F	65.7	54.4	59.6	63.3	61.2	60.2	54.2	46.40
Viscosity Index	82.5	99.4	90.9	86.0	88.8	89.9	100.1	111.7
Sulfur, wt %	1.19	0.10	0.37	0.71	0.24	0.13	0.06	0.01
Nitrogen, ppm	53	2	3	19	1.5	1	1.5	1.7
Boiling Range, °F								
1%	617	574	517	675	655	642	619	589
5%	749	698	751	801	778	766	731	635
10%	790	753	798	843	817	811	792	678
30%	849	891	907	871	873	871	886	806
50%	884	931	938	937	905	903	923	880
70%	916	966	968	967	936	935	955	924
90%	961	997	993	1008	982	982	999	974
95%	984	1009	1004	1023	1005	1005	1017	997

(1) Unit on standby over weekend hold off, pressure, H<sub>2</sub> flow, temperature unchanged).

Figures 1-5 are obtained from the data set forth in Table 3.

Referring to Figure 1, at 100 V.I., lube yield is about 80 wt.%, and at 110 V.I. yield drops sharply to 55 wt.%. The V.I. at 100 matches that obtained from premium lube stocks, such as Arab Light using conventional solvent dewaxing technology.

Referring to Figure 2, it can be seen that the 80% lube yield giving 100 V.I. corresponds to complete removal of the 17 wt.% sulfur compounds calculated to be in the chargestock. Thus, it appears the sulfur compounds in Arab Heavy have very low V.I., and their selective removal as accomplished by hydrotreating in this Example results in a fortuitous increase in V.I. to the desired 100 level. Conversion (hydrocracking) beyond this point gains some further V.I., but at a higher yield loss (Figure 1) and, as will be discussed later, loss of light and air stability.

Lube oil composition studies indicate that the major reaction occurring over the hydrotreating catalyst used herein as V.I. is increased from the 82.5 of the feedstock to 99.4 is desulfurization. The paraffins and naphthene contents increase in proportion to the removal of the 17% aromatic sulfur compounds calculated to be in the charge as shown in Table 4 below.



TABLE 4

Lube Composition Studies

Composition, wt.%	Charge				
	82.5 V. I. 100 wt.%	90.9 V. I. 91.6 wt.%		99.4 V. I. 78.9 wt.%	
	Found	Found Calc(1)		Found Calc(2)	
Paraffins	14.2	15.4	15.5	20.2	17.9
Mono Naphthenes	12.8	14.5	14.0	19.3	16.1
Poly Naphthenes	32.5	38.3	35.5	37.1	40.9
Aromatics (including S compounds)	40.5	31.8	35.0	23.4	25.1
	100.0	100.0	100.0	100.0	100.0

(1) Charge + 0.916 for paraffins and naphthenes, aromatics by difference.

(2) Charge ÷ 0.789 for paraffins and naphthenes, aromatics by difference.

If aromatics were being hydrogenated, the naphthene contents found would be higher than those calculated. At the 99.4 V. I. level essentially all the sulfur compounds have disappeared, so that further V. I. increase cannot be explained by desulfurization. The high hydrogen consumption at 111 V. I. (740 SCF/bbl (132 nl/l), Figure 3) indicates that aromatic hydrogenation does become significant after desulfurization is complete.

As shown in Figure 3, hydrogen consumption to make 100 V. I. oil over catalyst ICR-106™ is about 280 SCF/bbl (50 nl/l). Hydrogen consumption increases drastically as viscosity index increases to 110.

From Figure 4, it can be seen that the pour point remains substantially the same during hydrotreating within an experimental error of the charge,  $+25^{\circ}\text{F} \pm 5^{\circ}\text{F}$  ( $-4^{\circ}\text{C} \pm 2.8^{\circ}\text{C}$ ).

As shown in Figure 5, viscosities in SUS at  $110^{\circ}\text{F}$  ( $38^{\circ}\text{C}$ ) and  $210^{\circ}\text{F}$  ( $99^{\circ}\text{C}$ ) decreases with increasing V.I. The 100 V.I. oil, however, is still high in the SAE 20 viscosity index range of 45-58 seconds at  $210^{\circ}\text{F}$  ( $99^{\circ}\text{C}$ ).

### Example 3

Portions of the oils obtained from hydrotreating were exposed to air and sunlight for a period of three weeks. The 112 V.I. oil exhibited stability characteristics of hydrocracked oils, i.e. haze after 2 days exposure, and formation of suspended brown floc followed by precipitation after 4 days. The oils with 100 V.I. and less however, remain clear for 2-3 weeks which is generally considered sufficient to establish stability. However, haze and some solid matter do form from prolonged exposure. The results are shown in Table 5.

TABLE 5

### Air and Light Stability

Product V.I.		91	99	100	112
Charge		-3	-2	-7	-8
Days to Haze	50+	23	33	14	2
Days to Sludge	50+	50+	47	18	4
mm Sludge* at 10 days	0	0	0	0	<1
mm Sludge* at 50 days	0	0	<1	1	<1
				at 30 days	

\* Depth at bottom of vial

The haze in the 91 V.I. sample was a very fine divided white material as opposed to the reddish-brown coarse floc characteristic of hydrocracked oils. Warming of the oil by direct sunlight reduced the

haze considerably. An alcohol thermometer taped to the window read 115°F (46°C) while the room temperature was 78°F (26°C). Late in the day, as the oil cooled, the haze returned. This reversibility of the haze would fit wax formation. The charge oil containing all its aromatic sulfur compounds does not form haze, which suggests that the addition of sulfur compounds normally used in the additive package could inhibit the haze.

CLAIMS

1. A process for preparing a high quality lube basestock oil from waxy crude oil, which process comprises:

A) extracting a waxy crude oil distillate fraction that boils within the range from 316°C to 593°C (600°F to 1100°F), or a deasphalted short residuum fraction of said waxy crude oil, with an aromatic hydrocarbon solvent in order to yield a waxy raffinate from which undesirable compounds have been removed;

B) mixing the waxy raffinate with hydrogen and contacting the mixture at a temperature of 260°C to 357°C (500°F to 675°F) with a dewaxing catalyst comprising an aluminosilicate zeolite having a silica/alumina ratio of at least 12 and a constraint index of from 1 to 12, to thereby convert wax contained in the raffinate to lower boiling hydrocarbons; and

C) cascading the dewaxed raffinate to a hydrotreating zone wherein the dewaxed raffinate is contacted in the presence of hydrogen with a hydrotreating catalyst comprising a strong hydrogenation component on a non-acidic support, at a hydrogen partial pressure of from 6996 kPa to 20786 kPa (1000 psig to 3000 psig), at a temperature of from 260°C to 357°C (500°F to 675°F) and at a liquid hourly space velocity of from 0.1 to 2.0, thereby hydrotreating said dewaxed raffinate to effect substantially complete desulfurization of said dewaxed raffinate but to avoid substantial hydrogenation of aromatic compounds in said raffinate, in order to yield a lube basestock oil having a viscosity index of approximately 100.

2. A process according to claim 1 wherein the raffinate is prepared by extraction of a deasphalted short residuum fraction and wherein the total effluent of the catalytic dewaxing step is cascaded to the hydrotreating zone.

3. A process according to claim 1 or claim 2 wherein the dewaxing catalyst comprises an aluminosilicate zeolite selected from ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38, ZSM-48 or zeolite beta.

4. A process according to claim 1 or claim 2 wherein the dewaxing catalyst comprises ZSM-5 and a hydrogenation metal.

5. A process according to any of claims 1 to 4 wherein the raffinate is partially dewaxed by solvent dewaxing before the dewaxed raffinate is contacted with the hydrotreating catalyst.

6. A process according to any of claims 1 to 5 wherein the hydrotreating catalyst is supported nickel-tungsten or platinum on alumina.

7. A process according to claim 4 wherein the hydrogenation metal of the dewaxing catalyst is nickel.

Fig.1

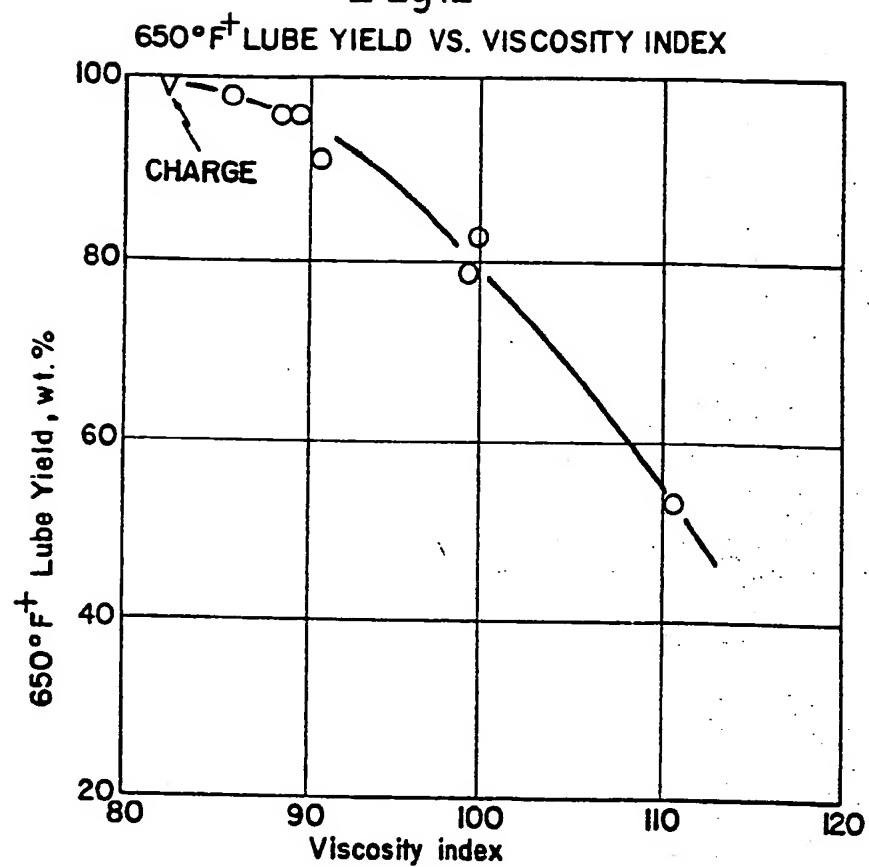


Fig.2

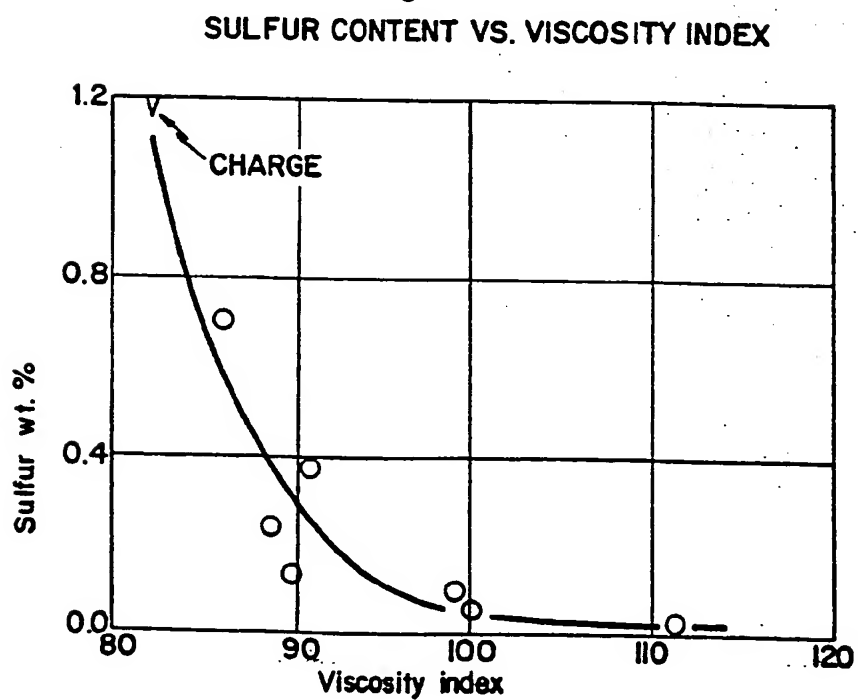


Fig. 3

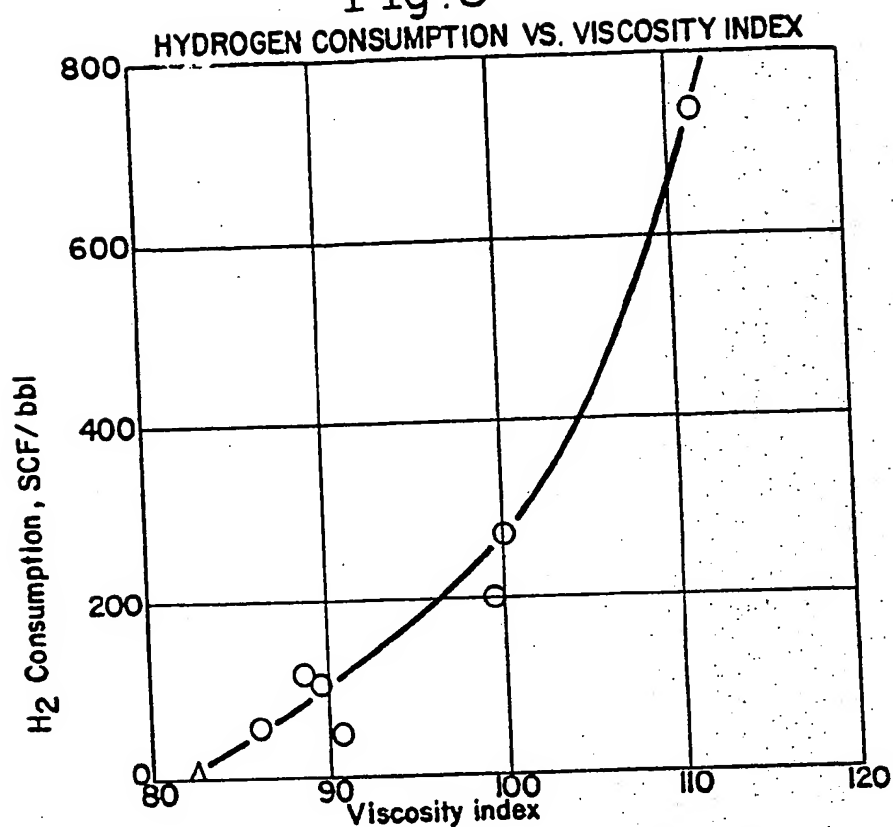


Fig. 4 POUR POINT VS. VISCOSITY INDEX

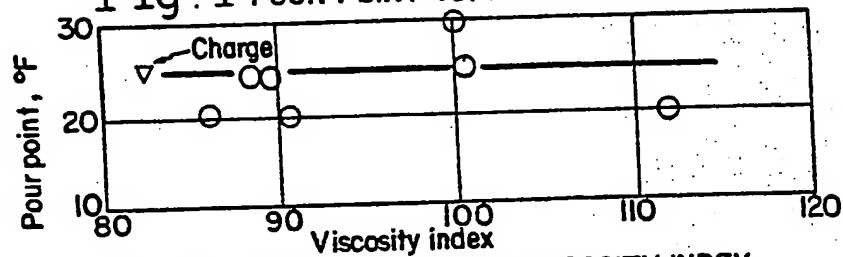
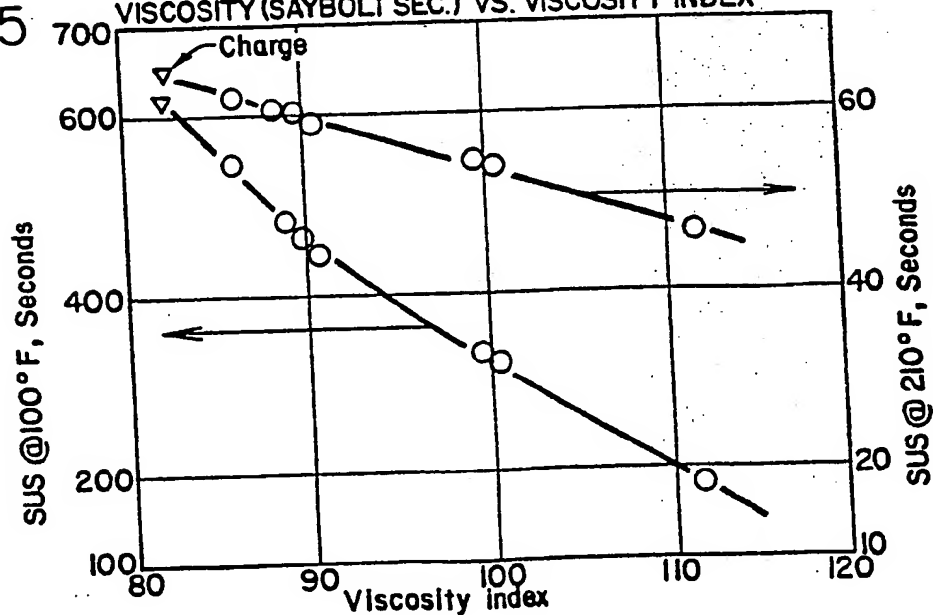


Fig. 5 VISCOSITY (SAYBOLT SEC.) VS. VISCOSITY INDEX





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# EUROPEAN SEARCH REPORT

0140468

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 84304382.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,X	<u>US - A - 4 181 598 (GILLESPIE et al.)</u> * Claims; column 2, line 60 - column 8, line 45 * -----	1,2,4,7	C 10 G 67/04
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 10 G 67/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 11-12-1984	Examiner STÖCKLMAYER
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	